

## Elemental, structural and optical properties of $Cd_{1-x}Co_xS$ thin films prepared by spray pyrolysis technique

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### Abstract

The  $Cd_{1-x}Co_xS$  ( $x=0.00, 0.10, 0.20$  and  $0.40$ ) thin films were deposited onto glass substrate at temperature 523K by using a low cost spray pyrolysis deposition (SPD) technique. The deposited films have been characterized their elemental, structural and optical properties measurements by energy dispersive X-ray, X-ray diffraction and UV-VIS spectrophotometer. Energy dispersive X-ray (EDX) analysis confirmed the presence of Cd, S and Co compositions in the films with appropriate stoichiometric. The as deposited films were amorphous in nature. The optical band gap of the films was decreased from 2.54 eV to 2.40 eV. Refractive index and the refractive index were affected by the doping concentration.

**Keywords:** SEM, spray pyrolysis, band gap and solar cell

### 1. Introduction

Cadmium sulfide (CdS) is a transparent metal sulfide semiconductor of the II-VI group compound semiconductors. Feitosa *et al.* (2004) reported that CdS has intensive attention due to their very important role on the photovoltaic technology, optoelectronic devices and solar cell fabrication. Archbold *et al.* (2005) examined that CdS is a hexagonal closed packed structure and has a wide band gap of 2.53eV, low resistivity and high transparency in the visible range and high light trapping characteristics. Several authors have been doped CdS with a wide variety of (F, Pt, Pb, Zn, Al, Co, In, Sn, etc.) elements to meet the demands of several application fields such as thin film solar cells ( Ristova and Ristov 1998), electrochemical cells (Jadhav *et al.* 2001), gas sensor (Kanemitsu *et al.* 2002) and it also has been employed in high efficiency solar cells formed with  $Cu_2S$  (Hall *et al.* 1979 ),  $Cu(InGa)Se_2$  (Nakoda *et al.* 1994), etc. Wu *et al.* (2006) proposed that CdS doped with transition metal ions (Fe, Ni, Mn ,Co and Cr), so-called dilute magnetic semiconductors (DMSs), such semiconductors offer the great opportunity to integrate the magnetic, electrical and optical advantages into a single semiconductor material, which provides many potential applications in the field of semiconductor spintronic and optoelectronic devices. Now a day's most of the semiconductors research is dedicated towards the fabrication of small-sized particle that includes the growth of semiconductor

nanocrystalline materials. These materials show a large optical band gap when the crystallite size becomes less than the Bohr exciton radius which is experimentally proved by Murray *et al.* (1995) & Mathur *et al.* (2004). Zenrui *et al.* (2002) found that CoS is an intrinsic semiconductor and a suitable candidate for photovoltaic or photothermal applications which has an optical band gap of 1.15 eV with cubic structure. Thus the alloying of Co with CdS may tune the optical band gap which may provide the suitability of this material for solar cells, optical window layers of photovoltaic cells, photodetectors, photoresistors etc applications.

In thin film preparation a variety of deposition techniques have been used to grow CdS and Co doped CdS thin films such as, chemical bath deposition (Zenrui, Yu *et al.* 2002 & Ezema *et al.* 2006), surfactant-assisted method (Sathyamoorthy *et al.* 2010), implantation-assisted method (Chandramohan *et al.* 2009), modified Bridgeman method (Lewicki *et al.* 1991), spray pyrolysis technique (Bacaksiz *et al.* 2008) etc. Spray pyrolysis deposition technique have also been considered as a viable technique for production of Co doped CdS thin films due to its many advantages over the conventional methods, viz., low cost experimental set up, high spatial selectivity, precise control over maneuvering the impurity concentration and possibility to overcome the solubility limit. In addition, this technique could be used for the production of large scale area for thin film deposition without employing any high vacuum system (Bedir *et al.* 2002).

In this work,  $Cd_{1-x}Co_xS$  thin films have been synthesized and investigated elemental, structural and optical properties by using EDX, XRD and UV-VIS spectroscopy.

## 2. Experimental

### 2.1 Preparation procedure

Figure 1 is a typical experimental setup for the preparation of  $Cd_{1-x}Co_xS$  thin films by the spray pyrolysis method. Aqueous solution of 0.1M cadmium acetate  $Cd(CH_3COO)_2 \cdot 3H_2O$ , 0.2M thiourea  $(NH_2CSNH_2)$  and 0.1M cobalt acetate  $Co(CH_3COO)_2 \cdot 4H_2O$  were taken as sources of Cd, S and Co. A considerable amount of (100 ml) solution was taken in the Beaker 'F' fitted with the spray nozzle 'A'. The clean substrate with a suitable mask was put on the susceptor of the heater 'H'. The distance between the tip of the nozzle and the surface of the glass substrate was kept 25 cm. The substrate temperature was kept at 523 K and was measured by placing a copper constantan thermocouple on the substrate. When compressed air is passed through 'P' (at 0.50 bar pressure) and at the same time water based precursor solution is feed at the nozzle A, then the solution sprayed and was automatically carried to the reactor zone upto 5 minutes where film was deposited onto the heated substrate.

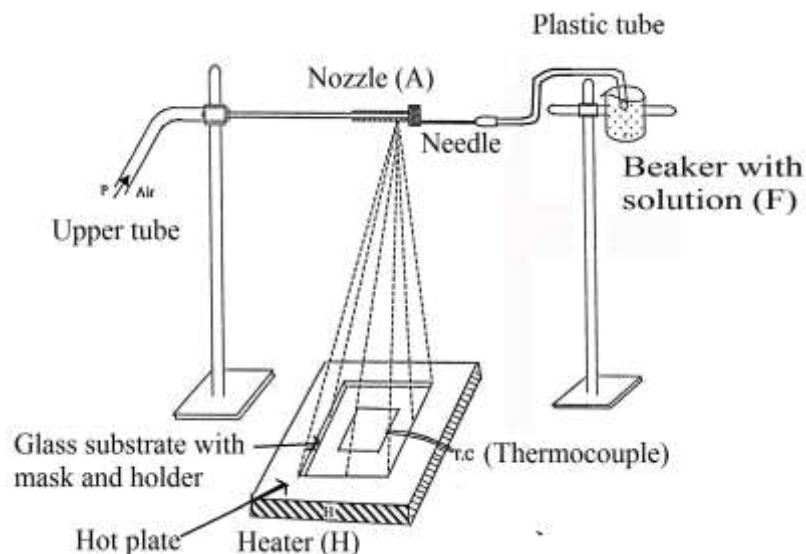
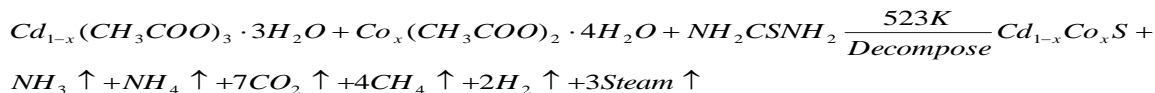


Figure 1. Experimental set up of spray pyrolysis method.

In the hot-zone, the atomized solution is dried and the constituent metal salts decompose and form intimate  $Cd_{1-x}Co_xS$  films. The possible chemical reaction may take place on the heated substrate as follows:



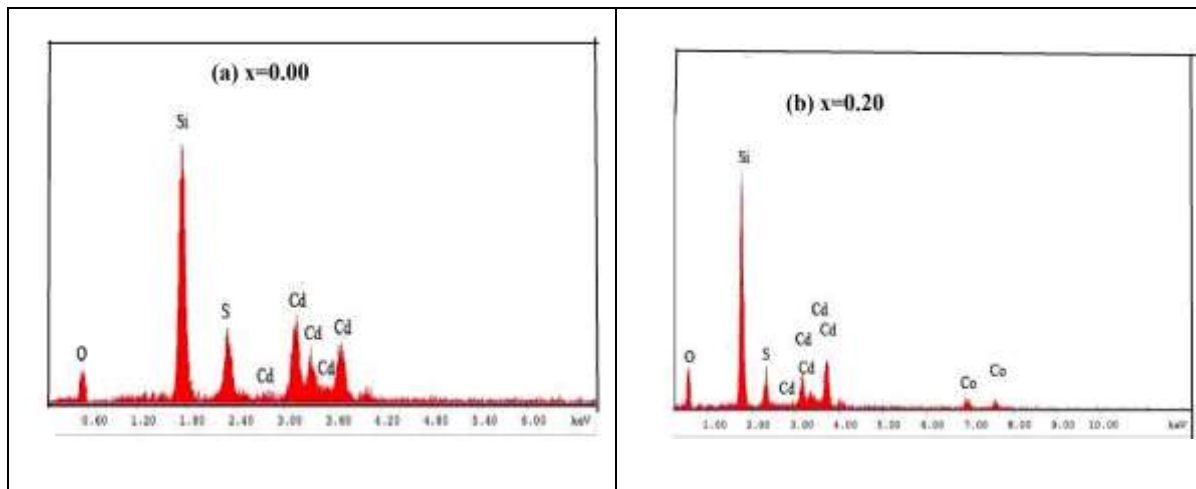
## 2.2 Characterization

The thicknesses of the films were measured by the setup of Fizeau fringes method at the department of Physics, BUET. Energy dispersive X- rays (EDX) were taken by the scanning electron microscopy (SEM) setup (Inspect IS50 FEI Company). The X-ray diffraction (XRD) of as deposited films were taken by using a molybdenum  $CuK_{\alpha}$  ( $\lambda = 1.54178 \text{ \AA}$ ), radiation diffractometer, PHILIPS model "X'Pert PRO XRD System. The optical absorbance and transmittance spectra of the as-deposited films with respect to plain glass substrate were taken at room temperature using double beam UV-VIS spectrophotometer (UV-1601PC Shimadzu, Japan) in BCSIR, for wavelength 300 nm to 1100 nm.

## 3. Results and discussion

### 3.1 Compositional Studies

The quantitative analysis of the films is shown in figure 2(a-c) and table 1 respectively.



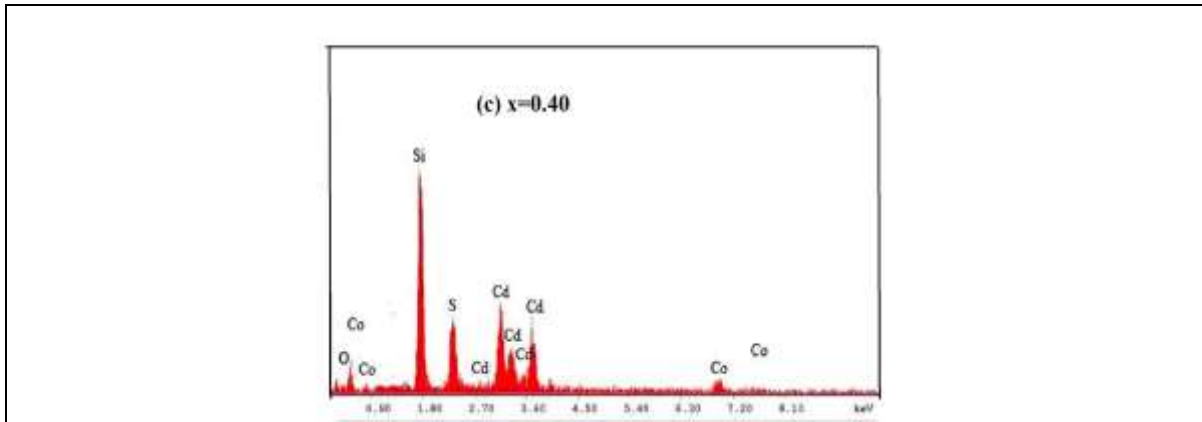


Figure 2. EDX spectra of  $Cd_{1-x}Co_xS$  thin films for (a)  $x = 0.40$ , (b)  $x = 0.20$  and (c)  $x = 0.40$ .

Some peaks are observed in figure 2 (a) that corresponds to Cd and S and confirms the CdS thin film. For  $x=0.20$  and  $0.40$  there have some extra peaks of Co in the spectra. It is worth to mention that the as-deposited  $Cd_{1-x}Co_xS$  films are stoichiometric. A silicon (Si) and an oxygen (O) strong peaks are also observed due to glass substrate. The decreasing of Cd peak height with increasing Co indicates the incorporation of Co. From table 1 it is evident that for all the films the amounts of Cd, S and Co are present in an excellent ratio.

Table 1. Atomic % for different compositions of  $Cd_{1-x}Co_xS$  thin films.

Compositions	Co atomic%	Cd atomic%	S atomic%
CdS	00	55.17	44.83
$Cd_{0.80}Co_{0.20}S$	12.59	37.35	50.06
$Cd_{0.60}Co_{0.40}S$	19.89	34.04	46.07

### 3.2 X-Ray Diffraction (XRD)

The X-ray diffraction patterns of pure CdS and Co doped CdS of as-deposited films as shown in fig. 3. Figure 3 shows that all the films contain a broad peak indicated the amorphous nature.

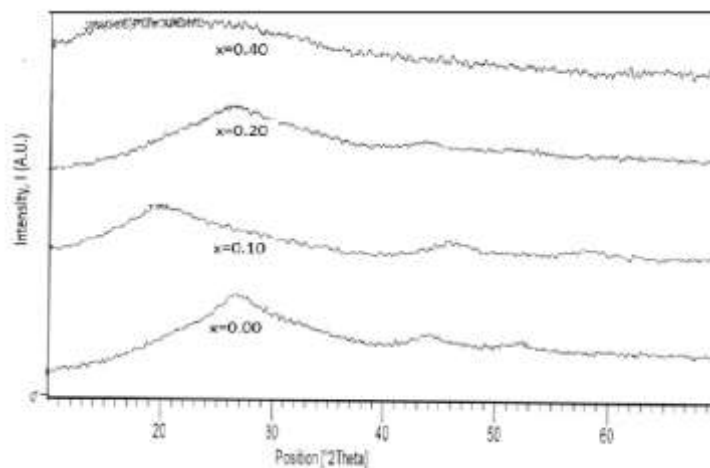


Figure 3. XRD spectra of as-deposited Cd<sub>1-x</sub>Co<sub>x</sub>S thin films.

### 3.3 Optical band gap

The absorbance and transmittance spectra of as-deposited films are shown in Figures 4(a) and 4(b). These spectra reveal that the films grown under the same parametric conditions have low absorbance in the visible and near infrared regions and are high in the ultraviolet region. However, absorption increases with increasing Co. Transmittance of all the films demonstrate more than 65% above wavelengths 550 nm and from 550 nm to 450 nm there is a sharp fall in the %T of the films, which is due to the strong absorbance of the films in this region. It has been observed that the over all %T decreases with Co content. This result is quite similar to that of the reported results of (Mathur *et al.* 2004 & Zenrui, Yu *et al.* 2002) film deposited by chemical bath deposition technique. The direct band gap energy of the films were determined from the  $(\alpha h\nu)^2$  vs.  $h\nu$  curve (figure 5). Band gap ( $E_g$ ) of the films decreases from 2.54 eV to 2.40 eV, which indicated that small amount incorporation of Co affects on the optical band gap. This reduction of the band gap is explained (Bacaksiz *et al.* 2008; Mishack *et al.* 2010 & Koidl 1977) by sp-d exchange interactions between the host material s-p band electrons and the localized d electrons of the Co ions.

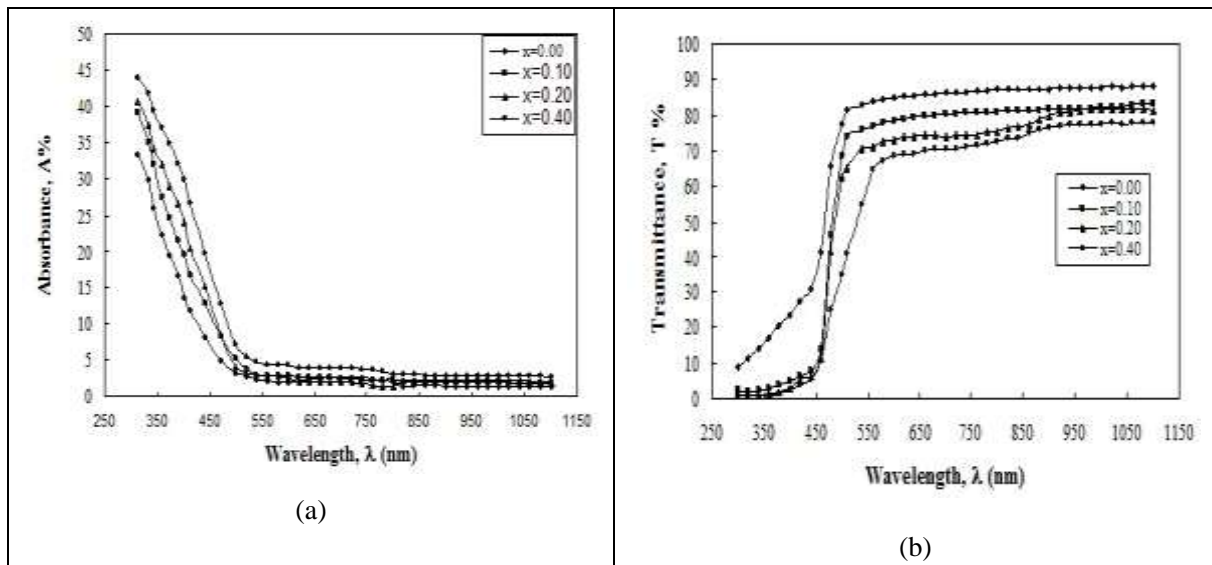


Figure 4. (a) Variation of absorbance and (b) transmittance as a function of wavelength of Cd<sub>1-x</sub>Co<sub>x</sub>S films.

This variation of the band gap energy may be useful to design a suitable window material in fabrication for solar cells.

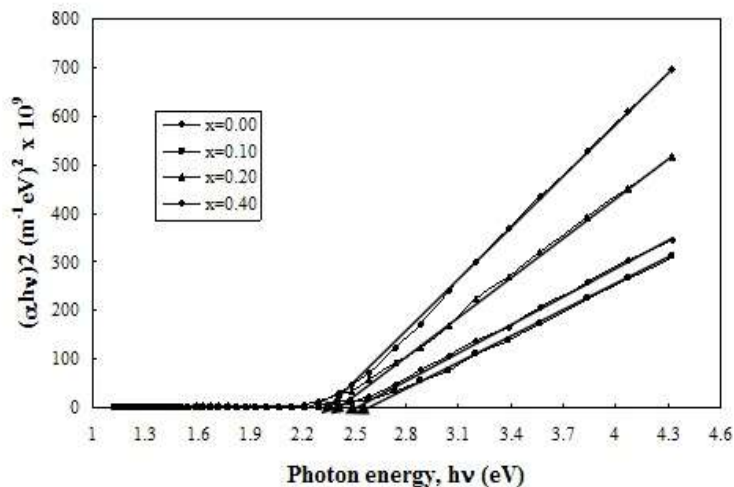


Figure 5. Plots of  $(\alpha h\nu)^2$  vs. photon energy  $(h\nu)$  for as-deposited  $\text{Cd}_{1-x}\text{Co}_x\text{S}$  thin films.

### 3.4. Extinction Coefficient

The extinction coefficient,  $(k)$  obtained from the relations (1) and (2)

$$k = \frac{\alpha\lambda}{4\pi} \quad (1)$$

and

$$\alpha = 2.303 \left( \frac{A}{d} \right) \quad (2)$$

where,  $\lambda$  is the wavelength and  $\alpha$  is the absorption coefficient,  $A$  is the optical absorbance and  $d$  is the thickness of the film. It is observed from figure 6 that the extinction coefficient falling with increasing wavelength from 300 to 500 nm. This may be due to the absorption of light at the grain boundaries. After wavelength 500 nm the value of 'k' remains constant.

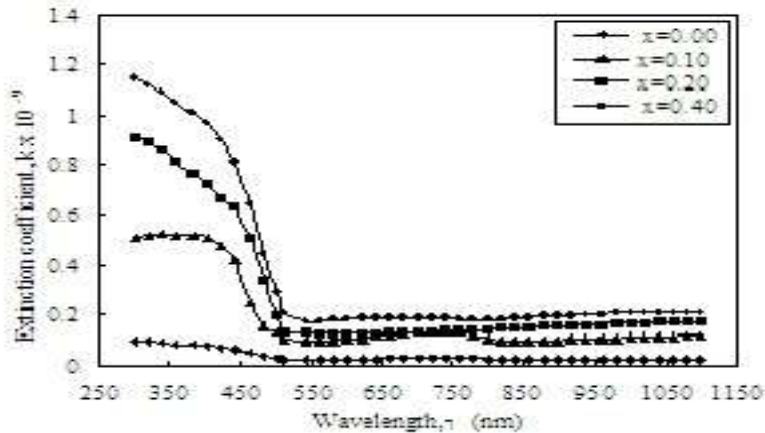


Figure 6. Variation of extinction coefficient as a function of wavelength for  $\text{Co}_{1-x}\text{Cd}_x\text{S}$  films.

### 3.5. Refractive Index

The refractive index,  $(n)$  of the films were determined using the relation (3)

$$n = \left( \frac{1+R}{1-R} \right) + \sqrt{\left( \frac{4R}{(1-R)^2} - k^2 \right)} \quad (3)$$

where,  $k$  is the extinction coefficient and  $R$  is the optical reflectance. The refractive index increases sharply in the wavelength between 300 to 480 nm which means it loses its energy, due to various loss mechanisms such as the generation of phonons, photo generation, free carrier absorption, scattering, etc.

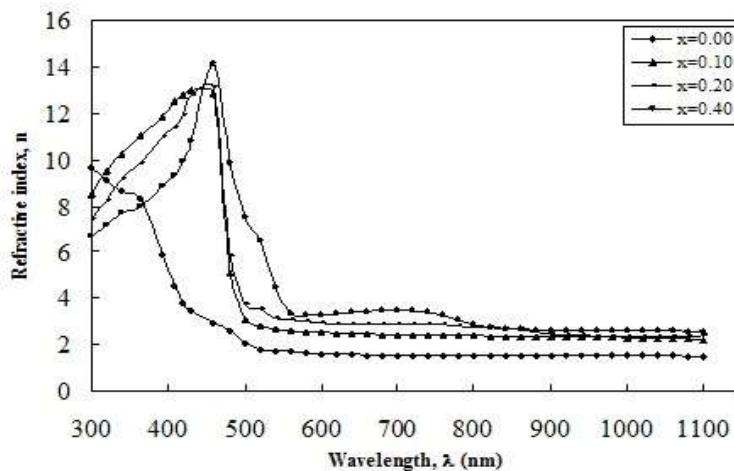


Figure 7. Variation of refractive index as a function of wavelength of the  $Cd_{1-x}Co_xS$  thin films.

The values of  $n$  decreases from 500 nm to 560 nm after that the value of 'n' remains more or less constant as shown in figure 7. The refractive index of the as-deposited films increases slowly with Co. So it is attributed to the variety of different impurities and defects.

#### 4. Conclusions

The amounts of Cd, S and Co are present in all the films with an excellent ratio. The as deposited films are amorphousness. The direct band gap energy of the films decreases from 2.54 eV to 2.40 eV. Extinction coefficient and refractive index tend to increase with increasing doping concentration. These optical values are appropriate for designing optical devices such as solar cells, optical window layers of photovoltaic cells, photo detectors etc.

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